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NIST

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Abstract

We have developed methods using Mass Spectroscopy, Liquid Chromatography and Gas Chromatography to detect degradation products of rag paper and newsprint in the presence of some common air pollutants. We have searched for products that might themselves be autocatalytic to encourage degradation of these materials. In particular, we have looked at gaseous degradation products and those degradation products which are mobile and which may be transferred from one paper to another by surface or gas phase diffusion .

Six organic acids have been tentatively identified as degradation products which are surface mobile on newsprint and rag paper. Acetic acid is a major organic acid gas phase component. The results of these studies were correlated with more traditional bulk paper properties tests.

SUMMARY

This report describes experiments in the accelerated aging of paper under static environmental conditions. The experiments were designed to measure effects of a relatively high pollutant concentration of 2500 ppm SO_2 at a slightly elevated temperature and humidity (air at 60°C and 25 percent relative humidity). These conditions may simulate long term effects of this common air pollutant usually found in ambient concentrations between 0.1 and 2.0 ppm. The samples were aged in parallel with and without added SO_2.

Samples of paper (newsprint and rag) were cut in the machine direction in strips 2 cm in width by 18 cm and placed in aging vessels fitted with an airtight septum cap in order to retain any volatile products of degradation. The septum caps were designed to permit intermittent withdrawal of gas specimens for gas chromatographic detection of volatile acids by flame ionization detection (GC-FID) or sulfur compounds by flame photometric detection (GC-FPD) prior to removal of the paper samples for physical and chemical testing. One objective in this project is to determine whether volatile products of aging may be detected, to identify them, and to determine their capabilites to accelerate aging rates. With SO_2 present, a trace of acetic acid was detected over the newsprint (but not rag) paper at the end of the first experiment by direct chromatographic analysis (GC-FID), i.e., without derivatization. It is not yet possible to relate generation of this volatile acid product to an aging mechanism or rate. Comparison with the calibration curve indicates a proportion of about 0.22 mole of volatile acetic acid per thousand moles of monosaccharide. Future tests with trace amounts of volatile acetic acid injected into such a closed vessel early in the aging process will indicate whether this acid product can function as an accelerator, possibly by promoting initial hydrolytic decomposition, or simply represents a stage in the decomposition.

GC-FPD on a silica gel column specifically treated to separate sulfur containing gases showed chromatographic resolution of two sulfur gases, one identified as SO_2, in the SO_2-treated environment over newsprint. High performance liquid chromatography (HPLC) on aqueous extracts showed eight peaks from the newsprint aged with SO_2, and six peaks in the absence of SO_2. Of the eight components found in newsprint aged in SO_2, six were tentatively identified as 2-ketoglutaric acid, malic acid, malonic acid, succinic acid, formic acid, and acetic acid. In the absence of SO_2, four acids were tentatively identified (malonic, succinic, formic and acetic acids). In the extract of rag paper there were only trace amounts of two species. These were tentatively identified as malonic and succinic acid.

Results of standard tests (fold, tensile, pH, and alkaline solubility) indicate extensive physical degradation of both papers at the end of 120 days of aging in the presence or absence of SO_2. Analysis of earlier data from this laboratory shows high correlation between changes in the chemistry of paper during accelerated aging (paper acidity and alkali solubility) and physical properties (fold, tensile strength, color reversion) with aging performed at four temperatures and four or five carefully controlled relative humidities in air or nitrogen. These correlations are probably traceable only to chain

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breaking in amorphous regions with concomitant decreases in the degree of polymerization. The chromatographic detection of fragments suggests a more fundamental characterization of aging steps.

Mass spectra indicate a new peak of apparent m/e = 38 in the atmosphere over both rag and newsprint. This unidentified peak suggests a volatile divalent fragment of mass 76, such as that of glycolic acid.

1.0 BACKGROUND

Protection of the records in the National Archives and Records Administration (NARA) from atmospheric pollutants has long been a concern. Recently a National Academy of Science committee was convened to study the problem of preservation of records in the NARA (1). In response to the National Academy of Science study, NARA supported the development of a research program by Elio Passaglia of NIST Polymers Division entitled "The Characterization of Microenvironments and the Degradation of Archival Records, A Research Program." (2)

The research program proposed by Passaglia divides itself into two major areas: (a) a study of the protection mechanism provided by containers, in particular, the cardboard boxes commonly used in safeguarding much of the archive materials; (b) a study of the degradation mechanism of paper and the relation of this degradation mechanism to various storage modes. This is a report on the methods developed to study the degradation products resulting from the degradation in the presence of pollutants.

To understand mechanisms of aging for a given paper in a given environment requires information on the course of complex degradative processes. Paper consists of a solid substrate that can vary greatly in the relative amount of alpha cellulose and hemicellulose, substituent groups on a cellulose chain, lignin content, morphology, filler, internal and surface sizing, retention aides, degradation products, pH, and trace metal content. Any of these may affect the activation energy for chemical and physical changes in aging over a range of temperatures. Conventional paper testing technology (fold, tensile strength, tearing resistance, etc) is designed to measure mechanical properties of sheet paper that may or may not be directly related to molecular changes (3). In this report we study both the products of the chemical degradation of paper and the mechanical testing of paper aged under the same conditions in an effort to relate the chemical degradation to the mechanical failure.

2.0 INTRODUCTION

In the past 50 years, many studies have been devoted to accelerated aging by heat and light, natural aging processes, and problems in comparing accelerated to natural aging. Theoretical papers and reviews (4,5,6) discuss the application of standard test methods to the determination of rates of change in properties under artificially severe conditions. The basic objective of aging under severe conditions is to save time by mathematically extrapolating the rate of the property obtained (e.g. physical failure) under severe conditions to the rate under natural conditions. Heat aging is the typical, though markedly disputed, choice. The Arrhenius equation is used

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extensively to extrapolate the data from results at high temperatures to predictions on aging at room temperature.

Ideally the rate of change "k" in a given property at a given (low or "natural") temperature "T" depends on a so-called activation energy "A", that has to be determined and expressed in units of energy. According to the Arrhenius equation:

$$d \ln k/(dT) = A/(RT^2)$$

From this equation the following is derived for two different temperatures:

$$-A/(2.303R) = \log(k_1/k_2)/(1/T_1 - 1/T_2).$$

That is, if one measures k at two different temperatures, the difference permits calculation of "A," and then one can estimate "k" for some other temperature. For paper as for many other materials in general, "k" refers to properties that may involve a number of concurrent or consecutive chemical reactions. Therefore, "A" is only an apparent constant. For such apparent constancy, the whole matter of comparisons becomes phenomenological, i. e., it is difficult to interpret the net process in terms of its detailed chemistry. The use of the Arrhenius equation may work out well empirically when the composition of a given paper and the environment are both well controlled, but in comparing different papers, complications enter (6), partly because of the inhomogeneity and the diversity of the substrate, and partly because few data exist to compare natural aging with the various accelerated aging conditions that have been devised.

In such accelerated aging, one can demonstrate high correlations between changes in the chemical and physical properties of laboratory handsheets of controlled composition without knowing exactly where the chemistry occurs. For example, decreases in fold and tensile strength both may be associated with decreases in the degree of polymerization in cellulose chains (7), but it has been suggested as well that degradation of "fines," a suspected colloidal carbohydrate material produced during paper manufacture, may have a major role in the chemistry of aging (7).

Increases in alkaline solubility, although they may appear before physical changes are evident (11), are nonspecific. Alkaline solubility may be affected by several events: chain degradation (12) to soluble fragments (e.g. carboxylic acids), changes in morphology, oxidation of hydroxylated carbons to carbonyls, thereby increasing the susceptibility to electron displacement mechanisms under alkaline conditions (13).

The situation becomes more complicated when papers of different manufacturers are compared. For example, Wilson has shown (6) that in natural aging the degree of correlations for changes in two given conventional properties is much higher for papers of similar composition, than for papers of dissimilar composition. Commenting on the use of the Arrhenius equation to predict aging properties of papers, Wilson concludes that "A far more useful approach should be to probe the (chemical) reactions that occur during natural aging and devise accelerated aging conditions that cause these same reactions to occur." Neimo in 1964 (13) stated that "accurate analysis of the structure

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of the disintegration products may be the only method by which a correct picture of the mechanism of aging can be obtained, but at present very little admittedly is known about the oxidation and disintegration products of cellulose."

Little aging of paper has been done at temperatures as low as 60 °C. We know of no studies on aging at 60 °C where the products of degradation have been studied except for the earlier study by Stubchen-Kirchner(14) on yellowing discussed below. Antal has reviewed the chemistry of pyrolysis of biomass at in three temperature regimes. From the degradation of alfa-cellulose in the temperature regime below 200 °C (all of the studies he discusses are at temperatures well above 60 °C), he reports degradation products consisting of low molecular weight ketones, aldehydes, acids (acetic and formic) and some phenols. Chatterjee also reports seeing similar products at higher temperature.

Two earlier studies have been directed at determining the degradation products under milder aging conditions. Stubchen-Kirchner (14) early recognized the promise of thin layer chromatography to separate and identify soluble carbohydrate moieties such as uronic acids which can promote yellowing, "color reversion" of paper, but the chromatographic techniques of the early 1960's lacked the sensitivity and specificity of ion chromatographic HPLC demonstrated in our recent work on the separation of acid fungal metabolites of glucose (15). As yet, Neimo's statement essentially still holds true for paper.

Erhardt et al. (16) took a novel and more fundamental approach to the study of chemical products resulting from accelerated aging tests. They used gas chromatography on derivitized components of aqueous extracts from artificially aged paper at 90 °C in both dry and humid atmospheres to characterize degradation in terms of the separable molecular fragments generated. They succeeded in showing a fundamental difference between molecular products of dry and humid aging at 90 °C or higher temperatures. While their aging conditions were undoubtedly severe, their work does suggest that a relatively simple, sensitive and accurate chromatographic method might strengthen the case for aging studies in paper technology by showing whether the same chemical products are obtained continuously over a set of aging conditions.

3.0 PURPOSE OF THIS STUDY

The degradation rate of the paper material can be either enhanced or reduced depending on storage conditions. For example, it has been suggested (and has sometimes been implemented) that the paper material be sealed in a plastic wrap which is impermeable to moderate molecular weight pollutants like SO_2, because such pollutants are known to promote degradation. However, this sealing not only keeps out the SO_2 but also keeps in many of the degradation products of the paper. These degradation products may help catalyze the degradation of the paper (autocatalysis).

Moreover, these degradation products may not only cause degradation to the paper they have come from but may also diffuse around the sealed container and act as a catalyst in the degradation of other papers. For example, an

unstable degrading newsprint sealed together with a more stable bond may speed the degradation of the bond paper as a result of the diffusion of degradation products.

Degradation products with significant vapor pressure at room temperature are kept in by the sealing of the papers within a container. The diffusion of these degration products can occur in a variety of ways. They may become air borne and attach themselves to another paper or to another site on the same paper encouraging degradation there. Species not air borne may diffuse on the surface of the paper--the surface of a porous material like paper includes regions "inside" the paper. Surface diffusion is often found to be very fast and thus movement on the surface may be expected to occur as rapidly as it occurs in the gas phase. For papers in contact, surface diffusion could allow degradation products to transfer from one piece of paper to another almost as easily as gaseous diffusion.

It is the purpose of this work to suggest and establish analytical methods to identify and quantify the major mobile decomposition products of paper under accelerated aging conditions. A GC and MS methodology has been designed to look at gas phase components of the degradation process. A liquid chromatographic method which includes extraction and washing of the paper with H_2O looks at both gas and surface mobile materials. In the present research, along with the chromatographic techniques described above, we have also used traditional physical tests on paper i.e., fold test, tensile strength, as another index of aging in properties and to compare our results with earlier data on paper.

To develop and test the chemical methods, we have chosen to look at two extreme forms of paper - rag and newsprint. For all the experiments reported here the environment is maintained at relatively low temperature (60 °C) and relative humidity (25%). To accelerate effects of pollution, we use an artificially high concentration (2500 ppm) of sulfur dioxide instead of the expected less than 1 to possibly 10 ppm common in a polluted city environment.

In our search for mobile decomposition products we have looked for those materials most likely to be effective as autocatalysts in the aging of paper. Since acid hydrolysis is the most probable degradation mechanism for paper and since aging generates acid products, organic acids of low molecular weight are of primary interest.

4.0 EXPERIMENTAL.

4.1 Samples. The paper samples were supplied by commercial manufactures: newsprint (Bowater Southern Paper Co, Calhoun TN), and 100

percent rag (Fox River Paper Co., Appleton WI)[1]. Properties measured by standard tests before and after aging are summarized in (Table 1).

4.2 _Aging apparatus._ Two baths were used in series (stainless steel, 30.5 by 35.6 by 30.5 cm deep, Lab-Line Imperial IV, Thomas Scientific, Swedesboro, New Jersey). One bath (prehumidifier) was maintained at a temperature of 45°C and the second (aging bath) at 60°C. Air was passed through sintered glass at the bottom of a 22-cm tall glass cylinder in the prehumidifier bath and through heated glass tubing (heating tape, variable transformer) at a temperature high enough to prevent condensation. To this stream of humid air was added either dry nitrogen at the same flow rate or dry SO_2 in nitrogen, again at the same metered flow rate. The mixture passed through a Teflon stopcock spliced on glass tubing into a coil of glass tubing wrapped around the aging vessel, and finally through the bottom of the pyrex glass aging vessel which contained suspended strips of paper. The top of the aging vessel was threaded to accommodate a Mininert-valve equipped cap (Supelco, Inc., Bellefonte, PA). At first the cap was loosely fitted on the vessel to allow the air/N_2 mixture to pass through the system for one hour of conditioning. Two of the vessels - one containing rag paper and one containing newsprint - were then sealed off at both ends by means of the stopcock and the septum fitted Mininert cap. For the other two, a mixture of SO_2 (5000 ppm) in nitrogen was substituted for the dry nitrogen, permitted to flow for fifteen minutes, and finally sealed off at the stopcock and the cap. All samples for gas chromatography were withdrawn into a syringe through the septum and replaced with the same volume of ambient air. Aging continued for four months at 60°C in these gases having, initially, a relative humidity of 25% relative humidity and either 2500 ppm of added sulfur dioxide, or none. All analytical methods described in this work are used on the papers aged in this aging apparatus.

4.3 _Measurements_

4.3.1 _Properties investigated by standard methods._ Folding endurance; ASTM Designation: D-2176-69. Tensile breaking strength: ASTM Designation: D-828-60. Hydrogen ion concentration (pH) of paper extracts (cold extraction method): Tappi test method T 509 om-83. One percent sodium hydroxide solubility of wood and pulp: Tappi test method T-212 om-83.

4.3.2 _Liquid Chromatography._

4.3.2.1 _Instrumentation._ High performance liquid chromatography was performed with a 4.8-mm by 50-cm column packed with divinylbenzene-cross-linked polystyrene (PS-DVB) having sulfonate substituents (Shodex ionpack C-811, Alltech Associates, Deerfield, IL); measured column efficiency 20,000 plates

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[1]Certain suppliers of chemicals and equipment are identified by name in order to specify the experimental conditions adequately. This does not imply endorsement or recommendation by the National Institute of Standards and Technology nor does it imply that the particular brands of chemicals and equipment named are necessarily the best for the purpose.

per meter. The detector was a Knauer UV/RI dual detector (Utopia Instruments, Inc., Joliet, ILL), UV absorption measured at 254 nm. The injection valve (Rheodyne model 7120, Berkeley, CA) was equipped with a 50-μL sample loop. The pump was a single plunger HPLC pump (Wescan Versapump III, Alltech Associates) with a stated flow range of 10 μL min^{-1} to 5 mL min^{-1} and a flow accuracy of $\pm$1%.

   4.3.2.2 <u>Sample preparation</u>. Paper samples (approx. 0.15 g) were placed in a test tube, macerated in 5-mL deionized water with a glass rod and extracted overnight at ambient temperature. The extract was filtered (0.22 μm pore size) and injected directly into the sample loop.   The eluent consisted of 0.035 % (v/v) perchloric acid in deionized water, with a flow rate of 0.5 mL min^{-1}, routinely degassed each day by stirring magnetically for a half hour or more under house vacuum. Degassing in this manner usually stopped the perturbation of chromatograms by air bubbles coming off the column. Authentic samples of carboxylic acids of the highest available purity were purchased commercially and used without further purification. About 0.01 g of each compound was dissolved in deionized water, diluted as necessary and injected (50 μL) without derivitization. Oat xylan is only partially soluble in water. Thus a sample was permitted to stand overnight, stirred, filtered (0.22 μm pore size), and injected without derivatization.

   4.3.3 <u>Gas Chromatography.</u>

   4.3.3.1 <u>Instrumentation.</u> To detect non-sulfur-containing volatile compounds over aged paper, GC was performed with a flame ionization detector (GC-FID) using a Hewlett-Packard Model 5700A equipped with a 30-meter Megabore column coated with acidified polyethylene glycol (DB-FFAP Megabore column, J & W Scientific, Folsom, CA). Other GC operating parameters are as follows: port, column, and detector temperature, 150 °C; air flow, 240 mL min^{-1}; hydrogen flow, 20 mL min^{-1}; N$_2$ carrier gas, 30 mL min^{-1}; and injection volume, 1 mL.

   For compounds containing sulfur (e.g. SO$_2$), a sulfur-selective flame photometric detector, GC-FPD was used. A Hewlett Packard Model 5730 GC-FPD was equipped with a 393-nm sulfur-specific filter. The injection port was maintained at 100 °C, and the oven at 40 °C. In order to achieve the detection threshold and avoid overloading the detector, injection volumes were varied (0.25 mL to 10 mL) according to the sulfur concentration measured.

   4.3.4 <u>Mass spectroscopy</u>. An Extranuclear quadrupole mass spectrometer was used to identify volatile gaseous products. Mass spectra were taken on 2-mL samples of gases collected over accelerated aging specimens (rag or newsprint at 60 °C, 25% RH, with and without SO$_2$). These samples were injected directly into a special on-line septum vessel connected by an inert valve to the MS system.

5.0 RESULTS

5.1 Liquid chromatography.

5.1.1 <u>Newsprint</u>. Figure 1 is the chromatogram of 50 μL of water. The single negative peak is due to the plug of water displacing the same volume of eluent (0.035% $HClO_4$ in water). Figure 2 is the corresponding chromatogram of unaged newsprint, and Figure 3 is that of newsprint aged for 120 days at 60°C and 25% relative humidity. Figure 4 is similar to Figure 3 but with the addition to the aging environment of 2500 ppm of sulfur dioxide. For Figures 3 and 4, the consecutive peaks are identified in Table 2 as acid carbohydrates.

The effects of aging on the chromatograms are remarkable. Aging at 25% RH produces a strong positive peak, like that of soluble oat xylan ($k' = 0.007$, Figure 5), but tailing, probably because the major soluble oligomer is degraded to smaller fragments. This peak appears too early to assign specifically and conclusively to xylan, but it is probably a structurally similar oligomer. The subsequent, lesser peaks are due to soluble decomposition products. The most abundant is malonic acid [$CH_2(COOH)_2$]. Succinic acid [$(CH_2)_2(COOH)_2$], formic acid (HCOOH), and acetic acid (CH_3COOH) all are present in trace amounts. The capacity factors are given in Table 2.

When SO_2 is added (Figure 4), the height of the narrow initial peak is diminished but a new peak appears ($k' = 0.06$) probably owing to a slight modification of the parent oligomer. Tailing is more severe than aging without SO_2, and there appears to be a shoulder ($k' = 0.23$) possibly due to oxaloacetic acid ($HOOCCH_2COCOOH$; $k' = 0.24$ for the authentic compound). Another shoulder ($k' = 0.26$) may be attributed to 2-ketoglutaric acid [$HOOCCO(CH_2)_2COOH$], and a new peak ($k' = 0.49$) to malic acid. The four subsequent peaks are identical to those found after humid aging in the absence of SO_2, but all of them have increased in height relative to the initial peak. Thus for newsprint, SO_2 probably accelerates the acid hydrolytic mechanism. The appearance of ketoacid peaks after hydrolysis in the presence of SO_2 may indicate that oxidation is somewhat promoted by SO_2, or simply that we see here a later stage of decomposition. These data strongly suggest using both higher and lower aging temperatures in the search for a meaningful accelerated aging condition.

5.1.2 <u>Rag paper</u>. The extract of the commercial rag paper as received (Figure 6), unlike newsprint, shows one strong peak corresponding in retention volume to a soluble oligomer such as xylan. The same paper aged in humid air displays traces of succinic and malonic acids (Figure 7), but little modification of the oligomer peak. With SO_2 added to the aging environment (Figure 8), the major peak is somewhat diminished in height, and broadened, but the chromatogram lacks the distinctive peaks of newsprint chromatograms. Future studies featuring a stepwise increase in the severity of aging conditions again are indicated in order to define a threshold beyond which any trends may become evident.

5.2 Gas chromatography with flame ionization dectector (GC-FID).

The results of GC-FID on 1-mL samples of the gases over aged papers are displayed in Figures 9 to 12. The chromatogram of air injected alone has a peak corresponding in retention time (36 seconds) to a strong peak found in air

collected over deionized water, and possibly a slight signal at 65 seconds. Essentially the same chromatograms result for gases collected over rag with or without SO_2 and over newsprint without SO_2. The gases over newsprint in the presence of SO_2 differ because they include traces of two materials eluting at 65 and 73 seconds. The first corresponds to acetic acid while the second as yet is unknown. In any event, triplicate analyses of the 4 samples and air gave reproducible peak magnitudes and retention times.

The FID detector for the GC is sensitive to carbon compounds and rejects most other elements. As expected we found no signal from SO_2. Furthermore, the column we used on the GC was designed to separate highly polar acids. Thus, less polar species like methane, ethanol or acetone showed no retention on the column. Thus the early peak which appears in most chromatography is likely unretained carbon bearing gaseous materials. The fact that this peak is particularly large in the newsprint degradation suggest that a number of unretained carbon bearing material are being detected. Figure 12 is a calibration plot for acetic acid sampled from saturated air and quantitated against peak heights. Acknowledging the relatively poor linear correlation (r = 0.967 in the figure), the peak height for the 300-mL volume of gas over newsprint corresponds to a total mass of 13.2 μg, or 0.22 μmole. Assuming for convenience that newsprint consisted entirely of a hydroglycosidic oligomers having a monomer molecular weight of 162, the four grams of paper comprise 0.22 μmole of monomer and the molecular ratio of volatile acid to monomer is 1:1000. However, the absence of acetic acid from the environment of rag suggests that the decomposition products of newsprint result from carbohydrate oligomers other than alpha cellulose, e.g. xylans or glucans.

It is reasonable to infer from these data that traces of volatile acids are generated during the aging of paper, but not that volatile acids can autocatalyze degradation. Earlier data have indicated that nonvolatile acids generated in open systems do not do so (10). Additional experiments will be required to investigate possible rate effects when volatile acids such as acetic acid are injected into the closed aging chamber containing paper.

5.3 <u>Mass Spectrometric results</u>.

5.3.1 <u>Aging at 60°C for 20 days</u>.

5.3.1.1 <u>Background.</u> The instrument background was run and subtracted from later runs.

5.3.1.2 <u>Newsprint with SO_2</u>. Expected gases, like nitrogen, carbon dioxide and water, are seen in the spectra. SO_2 (mass 64) is not found in this atmosphere after prolonged aging. This result is consistent with the GC-FPD results. No peak of higher mass is found, but the very strong peak of m/e = 38 is present and exceeds in intensity CO_2 (m/e = 44). Since CO_2 is an expected degradation product of cellulose, this is somewhat surprising. It is not at all clear what is responsible for the large m/e = 38 peak. For example, if the apparent mass of 38 represents a divalent fragment, its actual mass would be 76. Glycolic acid - $HOCH_2COOH$ - has that formula weight, for example. However, glycolic acid was not detected in the HPLC chromatograms of newsprint aged at 60 °C. This preliminary experiment needs to be duplicated.

5.3.1.3 <u>Newsprint without SO_2</u>. In the apparatus which was prepared with newsprint and air only, again a peak of m/e = 38 is prominent and exceeds that of CO_2. It is potentially very interesting that the m/e = 38 peak appears after aging at either 90 °C or 60 °C, as it would if the degradation processes were the same at both temperatures.

5.3.1.4 <u>Rag paper with and without SO_2</u>. Again, the spectra are nearly the same, both containing pronounced peaks at mass 38 but without other distinctive characteristics. Small amounts of SO_2 are found in the atmosphere of the apparatus initially containing SO_2 consistent with the GC-FPD results.

5.4 Sulfur Oxides Determinations

Sulfur dioxide absorbed into paper from the atmosphere is a suspected precursor of <u>in situ</u> acid hydrolysis through the formation of sulfurous acid, sulfuric acid or possible analogues with anhydrocellulose units. Consequently, an important objective in the present work is to determine the rate and quantity of sulfur compounds introduced into paper from the atmosphere. As reviewed by Wilson, the limited information available suggests an acceleration of physical deterioration (aging) by atmospheric SO_2 in a humid environment (6). The microanalytical chemistry for determining sulfates and related compounds in paper is sparse, although some success with radioactive materials has been reported (16). Consequently we have investigated several published methods for determining sulfate in hydrocarbons, so far with limited success.

5.4.1 <u>Turbidimetry.</u> The method is an adaptation of an ASTM procedure, "Standard Test Methods for Sulfide in Water"(17). In principle, sulfate in aqueous solution is treated with barium chloride under controlled conditions to produce a suspension of barium sulfate. The absorption is measured at 540 nm or, with more sensitivity, at 390 nm. A calibration curve that we prepared for the concentration range of 0 - 40 μg of sulfate in 2 mL of water showed a minimum detection limit of 0.55 μg, as calculated by the method of Parris et al. (18).

Samples of paper (Whatman No. 1, 0.5 g) were treated with aqueous sulfate (0 - 2.0 mg/g) as calcium sulfate, dried, macerated in 6N nitric acid, permitted to stand overnight, filtered through sintered glass, and washed (deionized water) to a total volume of 50 mL of clear fluid. The filtered solutions were tested for turbidity at acid pH (1.17) and neutral (7.5).

All of the samples were equal to the blank in turbidity. The failure to quantitate sulfur may be due either to incomplete removal of sulfate from paper, adsorption on glass, or interference in the test reaction caused by undetected organic materials in the clear solutions, such as the soluble xylans apparent in the liquid chromatograms of rag paper (cf Figure 6).

5.4.2 <u>Titrimetry</u>. The measurement of total sulfur in paper would obviate suspected side reactions. A method is available in the Leco combustion procedure (19), in which sulfur is volatilized and measured as a function of its iodine titre. However, the method is designed for relatively small samples (20 mg) with relatively high proportions of sulfur (parts per thousand) and

failed to detect the parts per million or lower concentrations that we are required to quantitate in paper.

5.4.3 <u>Colorimetry</u>. A number of papers describe the quantitation of sulfate in various organic substrate as a function of the reaction with barium chloranilate (20 - 24). The method depends on the reaction of the sulfate with barium and quantitation of the chloranilate chromophore, which is released into solution. The absorption is measured at 540 nm, or preferably at 332 nm (24). Cations can interfere by forming insoluble chloranilates (23) and are therefore removed by ion exchange chromatography (e.g. Amberlite resin IR-120, or one of many equivalent commercial resins).

We found this method far more sensitive to changes in sulfate concentration than turbidimetry, although the lowest detectable amount (0.6 μg) is the same. Again, however, the response to extracts from Whatman No. 1 filter paper doped with $CaSO_4$ was not concentration dependent, even after chromatographic removal of cations. The absorption of the blank was as intense as that of samples. Again this suggests that anions other than sulfate displace chloranilate from the barium salt. Identification and/or removal of the unknown interfering materials will be necessary for routine application of this very sensitive method for determining sulfate in paper.

5.4.4 <u>Gas Chromatography with a Flame Photometric Detector. (GC-FPD)</u>.
Since the technique (GC-FPD) is sulfur selective (25), it is potentially useful for quantitating the depletion of SO_2 from the atmosphere contained in closed aging vessels, a highly important objective in the present research. Measurements of ppm concentrations of SO_2 are reproducible to ± 5%.

5.4.4.1 <u>GC-FPD Analysis of rag and newsprint.</u> Analyses of sulfur gases by FPD sulfur-specific detection provide an important pathway in advancing our understanding of the mechanisms of paper degradation. We observed a significant difference in SO_2 uptake in newsprint versus rag. After 20 and 43 days of aging (60°C and 25% RH) less than 90% of the sulfur dioxide has been lost to adsorption and/or chemical reactions in the container with rag paper (2500 ppm SO_2). However, greater than 90% of the SO_2 (2500 ppm) in the atmosphere over the newsprint was lost to adsorption/reaction processes.

These results are consistent with those reported by Hudson and Milner (26), but only represent preliminary findings. More controlled experiments must be carried out for uptake rate and quantatition data.

Whereas Hudson and Milner used radioactive sulfur dioxide in their studies, our analytical technique affords us the opportunity of rapid analysis of SO_2 concentrations during long term experiments at trace levels. Since only 0.1% of the environment is used per analysis, the concentration of reactants in our apparatus will not be significantly perturbed. In our new aging experiments, we will monitor the adsorption of SO_2 throughout the course of the experiment.

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6.0 CONCLUSIONS

We have developed a methodology to look for degradation products in the presence of pollutants and without pollutants of paper and paper products. We have searched for products that might themselves be autocatalytic to encourage degradation of these materials. Further, we look for those products which are mobile and which may be transferred from paper to paper. Perhaps a product from one that degrades easier allows the degradation products to be transferred from one material which degrades to another which does not.

Our experiments suggest the following preliminary conclusions:
1. Physical (fold, tensile strength) and chemical tests (pH, alkaline solubility) show that two papers - rag and newsprint- are extensively degraded after 120 days at 60°C and 25% RH in a closed system with or without added SO_2
2. Chemical products of aging can be detected by either gas or liquid chromatography and by mass spectroscopy.
3. Liquid chromatography tentatively detects at least six organic acid products of newsprint and fewer of rag.
4. Gas chromatography detects a trace of volatile acetic acid over newsprint.
5. Mass spectroscopy shows the presence of an unidentified volatile fragment of apparent mass 38 (if monovalent) or 76 (if divalent) over both newsprint and rag.
6. Analysis of published data shows high correlations between changes in physical and chemical properties of papers of closely controlled composition aged under closely controlled conditions of temperature and humidity.
7. Such results, unlike HPLC results, are chemically nonspecific.
8. The present results suggest that future experiments could be devised to show continuity or discontinuity in the aging process over a broad range of temperatures
9. The result of such experiments could represent a major contribution to the theory and practice of accelerated aging.

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TABLE 1

Standard Paper Properties[*]

	pH[1]	Alkaline[2] solubility (%)	Folding[3] endurance (doublefolds)	Tensile[4] strength
Newsprint				
Unaged	5.0	0.0513	282.4	7.1
Aged (air)	4.3	0.1969	4.9	4.5
Aged (SO_2 in air)	3.9	0.2690	1.9	4.0
Rag				
Unaged	5.71	0.0094	85.1	17.1
Aged (air)	5.23	0.0255	34.0	14.6
Aged (SO_2 in air)	4.67	0.0349	10.5	14.7

[1]Using Tappi method T-509-om-832 average of 2 analyses.

[2]Using Tappi method T428 pm 77, average of 2 analyses, reported as %SO_3.

[3]Using ASTM method D2176-69 (600 gm load on newsprint, 1000 gm load on rag), 10 analyses each.

[4]Using ASTM method D828-60, 10 repeat analyses each.

[*]For each test method, ASTM or Tappi experimental procedures were followed except for minor changes. For alkaline solubility only 20% or less of the recommended weight (5g) was available for each test.

TABLE 2

Identification of Peaks in Chromatograms of
Aqueous Extract from Newsprint*

k' for 25% RH	k' for 25% RH + SO_2	Nearest Authentic Peak	
		k'	Compound
0.007	0.007	0.007	Dextran
0.06	0.06	-	Unknown
-	0.26	0.25	α-ketoglutaric acid
0.49	0.47	0.49	Malic Acid
0.56	0.56	0.54	Malonic Acid
0.84	0.84	0.85	Succinic Acid
0.99	1.00	0.99	Formic Acid
1.15	1.16	1.16	Acetic Acid

* k' is the liquid chromatographic value known as the capacity factor.

TABLE 3

Concentration of Eluites in Aqueous Extract of Aged Paper,
Estimated from Chromatograms

Eluite	Concentration (moles per thousand anhydroglucose units)			
	Newsprint		Rag	
	SO_2	No SO_2	SO_2	No SO_2
Xylan	6.13	7.80	24.08	23.65
Unknown	6.33	NS	NS	NS
α-ketoglutaric acid	1.98	NS	NS	NS
Malic acid	3.22	NS	NS	NS
Malonic acid	16.20	9.40	2.33	1.72
Succinic acid	4.21	3.84	NS	0.87
Formic acid	14.09	14.09	NS	NS
Acetic acid	19.26	10.08	NS	NS

Note: The unaged samples show no signals in the HPLC at the positions defining these compounds.

NS means no observed signal in the HPLC at the position defining this material.

Legends for Figures.

1. HPLC chromatogram of deionized water injected onto an ion exchange column. Injection volume 50 μL. Eluent 0.035 percent (v/v) $HClO_4$ in deionized water. Flow rate 0.5 mL min^{-1}. Detector, Knauer RI/UV Dual detector. RI sensitivity 1 x 10^{-7} RIFS. UV sensitivity 0.0125 AUFS. Chart speed 0.5 cm min^{-1}.

2. HPLC chromatogram of aqueous extract (overnight, ambient conditions) of unaged newsprint, 0.15 g in 5 mL of deionized water, filtered (0.22 μm pore size). Negative RI peak is deionized water from extraction technique. Operating parameters as in Figure 1.

3. HPLC chromatogram of filtered, aqueous extract of newsprint aged for 120 days at 60 °C and 25 % relative humidity in a closed vessel. RI peaks are (a) xylans (e) malonic acid (f) succinic acid (g) formic acid (h) acetic acid. Sample treatment and instrument parameters are as for Figure 2.

4. HPLC chromatogram of filtered, aqueous extract of newsprint aged for 120 days at 60 °C and 25 % relative humidity with 2500 ppm of SO_2 added to the aging environment. RI peaks are (a) xylans (b) unknown degradation product (c) α-ketoglutonic acid (d) malic acid (e) malonic acid (f) succinic acid (g) formic acid (h) acetic acid. Sample treatment and instrument parameters are the same as Figure 2.

5. HPLC chromatogram of oat xylan saturated in water and filtered. Experimental parameters are as in Figure 2.

6. HPLC chromatogram of filtered aqueous extract of unaged rag paper. RI peak is Xylans. Parameters are as in Figure 2.

7. HPLC chromatogram of filtered, aqueous extract of rag paper aged for 120 days at 60 °C and 25 percent relative humidity in a closed vessel. RI peaks are (a) xylans (e) malonic acid and (f) succinic acid. Sample treatment and instrument parameters are as in Figure 2.

8. HPLC chromatogram of filtered aqueous extract of rag paper aged for 120 days at 60 °C and 25% relative humidity with 2500 ppm of SO_2 added. Sample treatment and instrument parameters are as for Figure 2.

9. Background. gas chromatogram with flame ionization detector (GC-FID) of ambient air. 1.0 mL injected into acidified polyethylene glycol coated 3-meter long megabore column. Gas flow: nitrogen, 30 mL min^{-1}; hydrogen, 20 mL min^{-1}; air, 240 mL min^{-1}. Injection port, column and detector are all at 150 °C.

10. (a) Gas chromatogram of atmosphere over rag paper aged (closed vessel, 60 °C) for 120 days. GC-FID parameters are as in Figure 9.

    (b) Gas chromatogram of atmosphere over rag paper aged (as above), with addition of 2500 ppm SO_2. GC-FID parameters are as in Figure 9.

11. (a) Gas chromatogram atmosphere over newsprint aged as in Figure 10(a). GC-FID parameters as in Figure 9.

    (b) Gas chromatogram atmosphere over newsprint aged with added SO_2, as in Figure 10(b). GC-FID parameters as in Figure 9.

12. Calibration curve obtained with known amounts of volatile acetic acid. GC-FID conditions as in Figure 9.
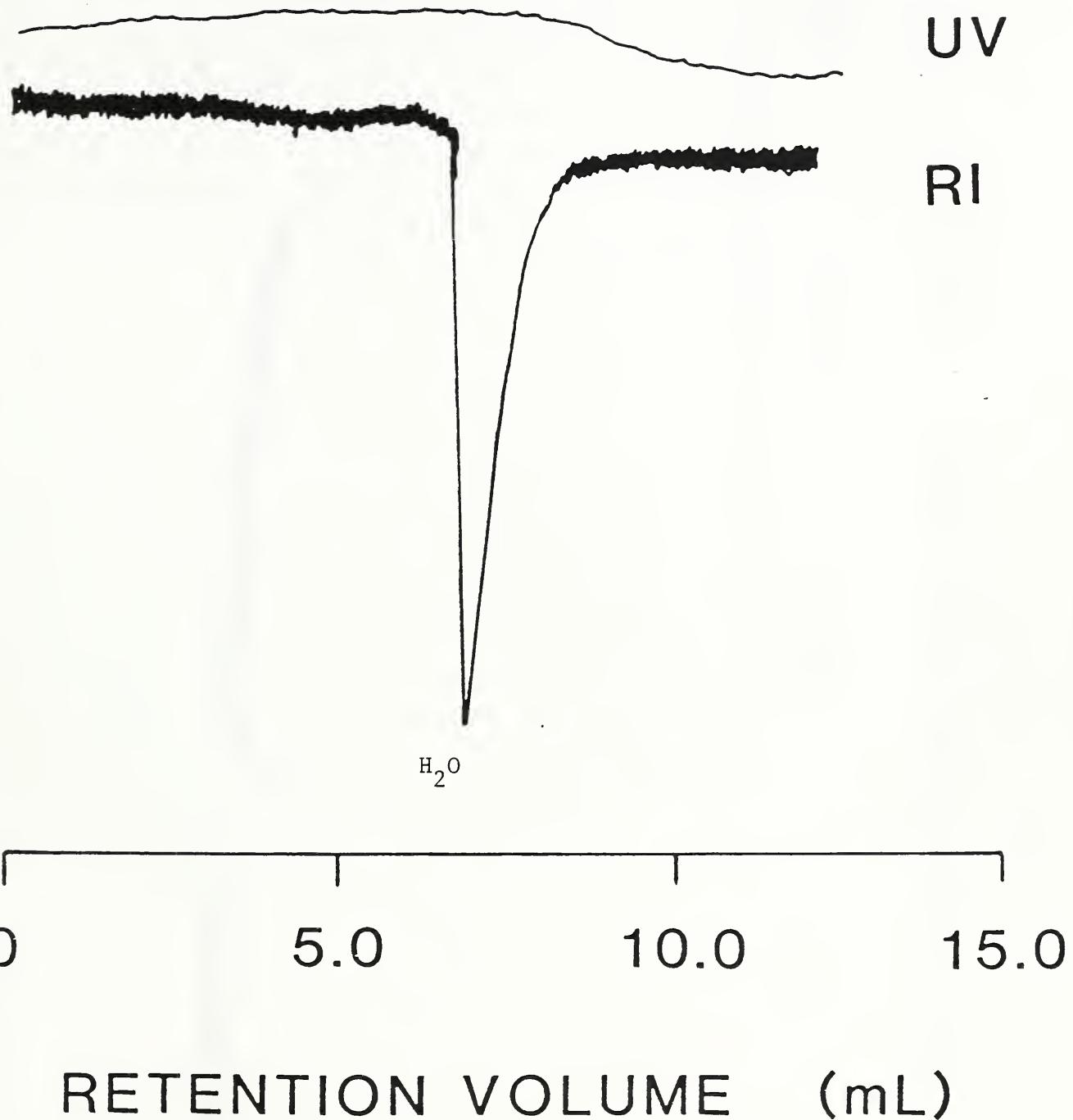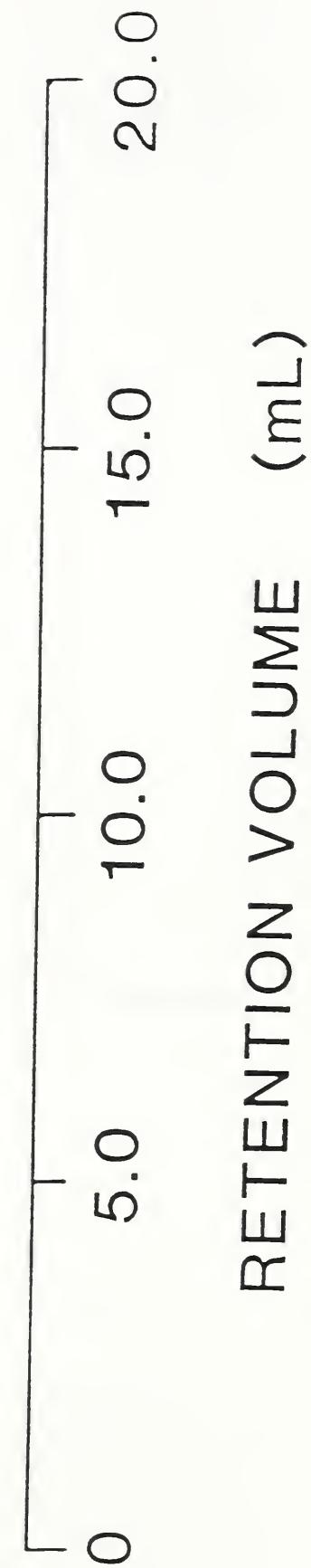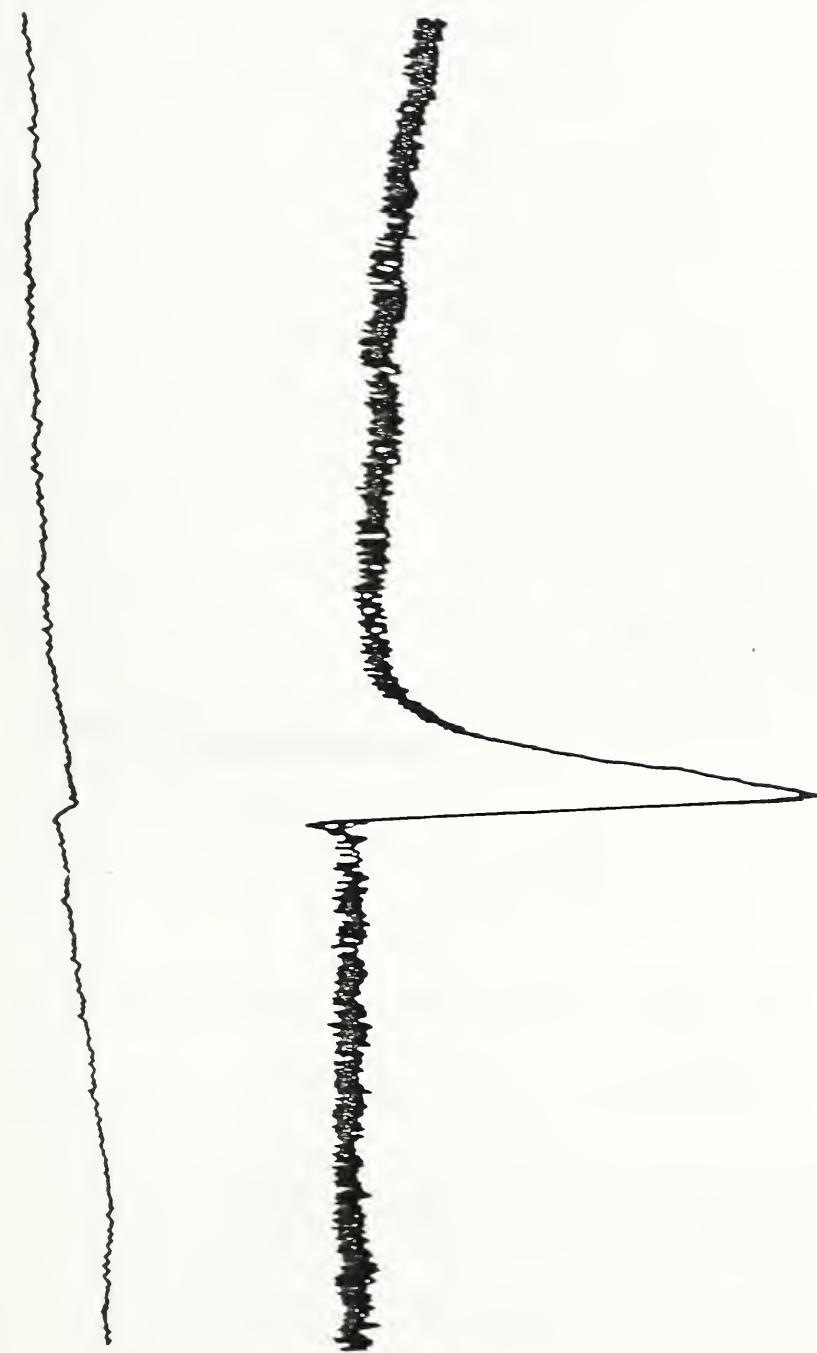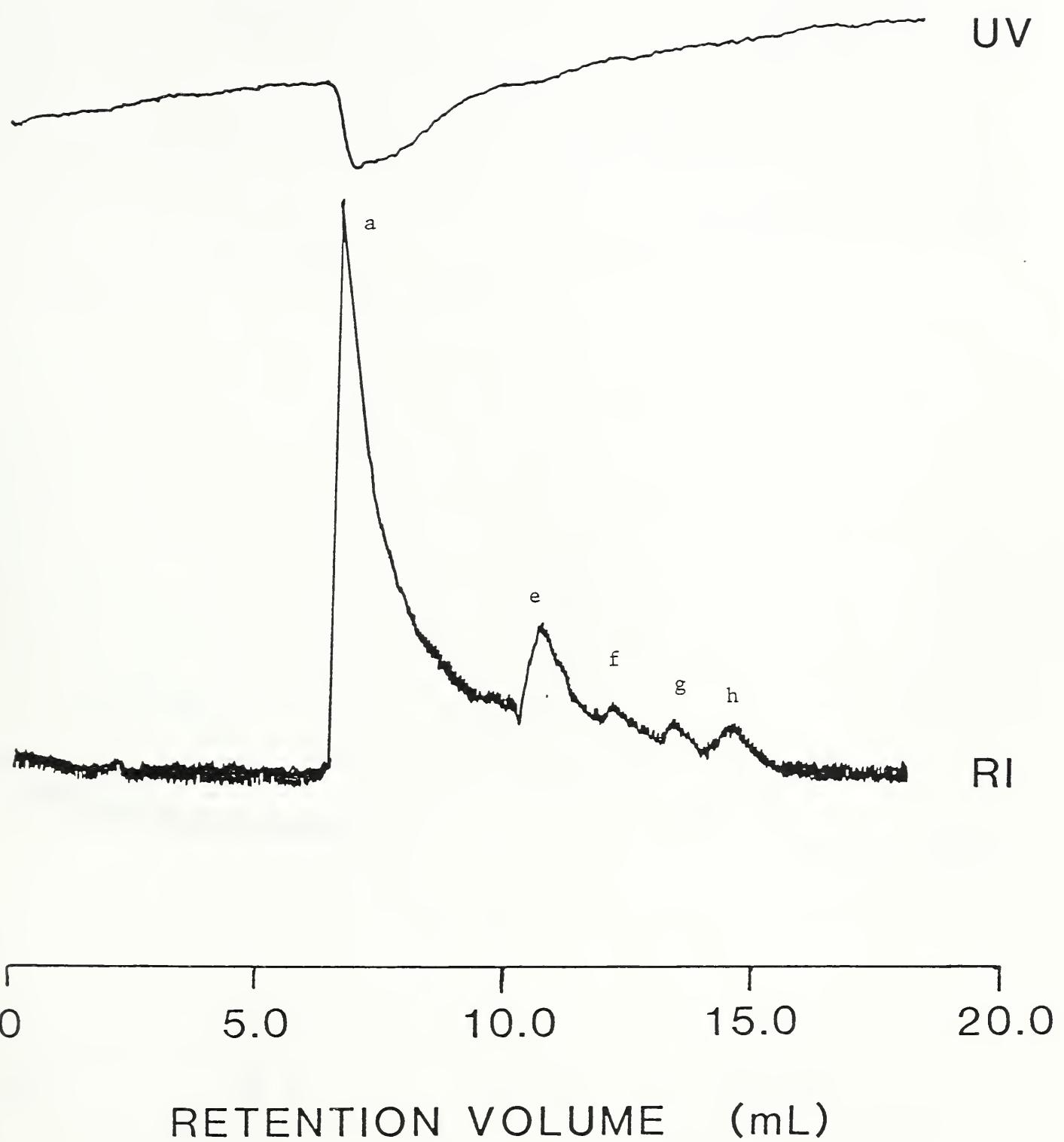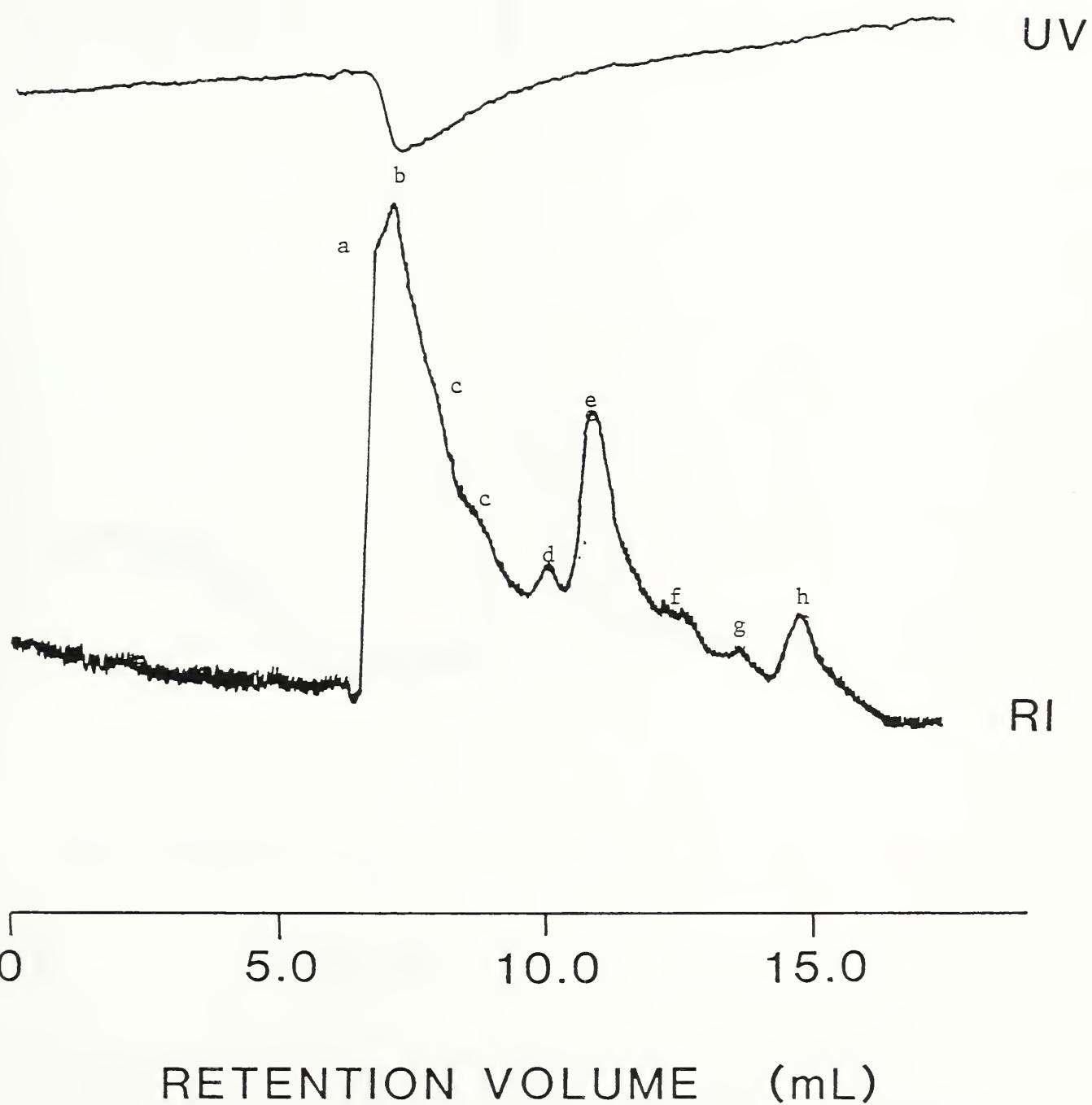
UV

RI

H$_2$O

RETENTION VOLUME (mL)

0   5.0   10.0   15.0

Figure 1

21

Figure 2

UV

RI

RETENTION VOLUME (mL)

20.0

15.0

10.0

5.0

0

23

Figure 3

25

Figure 4

UV

RI

0   5.0   10.0

RETENTION VOLUME   (mL)

Figure 5

29

UV

RI

0   5.0   10.0   15.0   20.0

RETENTION VOLUME   (mL)

Figure 6

31

UV

RI

0   5.0   10.0   15.0

RETENTION VOLUME   (mL)

Figure 7

UV

RI

0   5.0   10.0   15.0

RETENTION VOLUME   (mL)

Figure 8

RETENTION TIME (min)

Figure 9

RETENTION TIME (min)

Figure 10

Figure 11

41

Figure 12
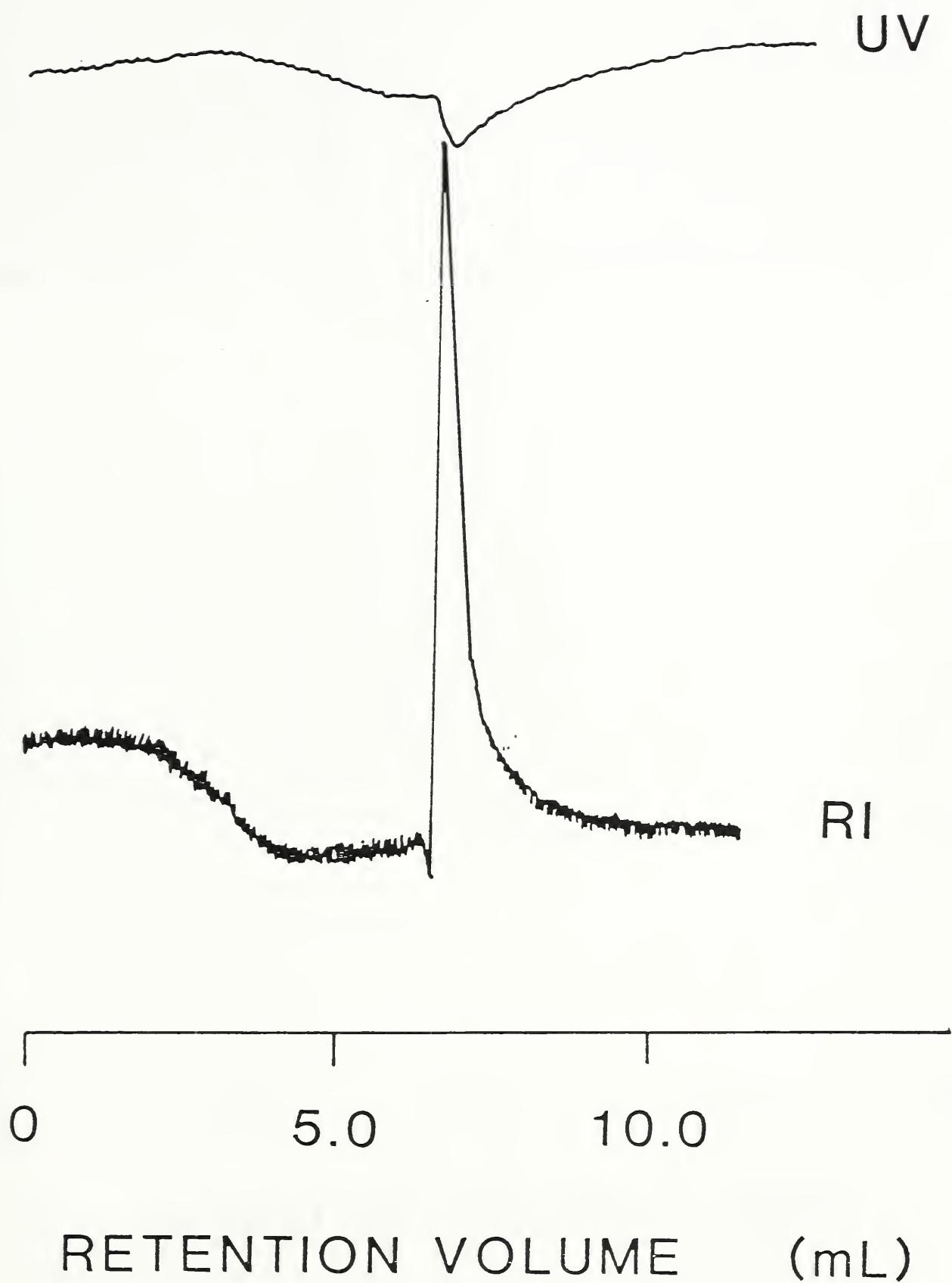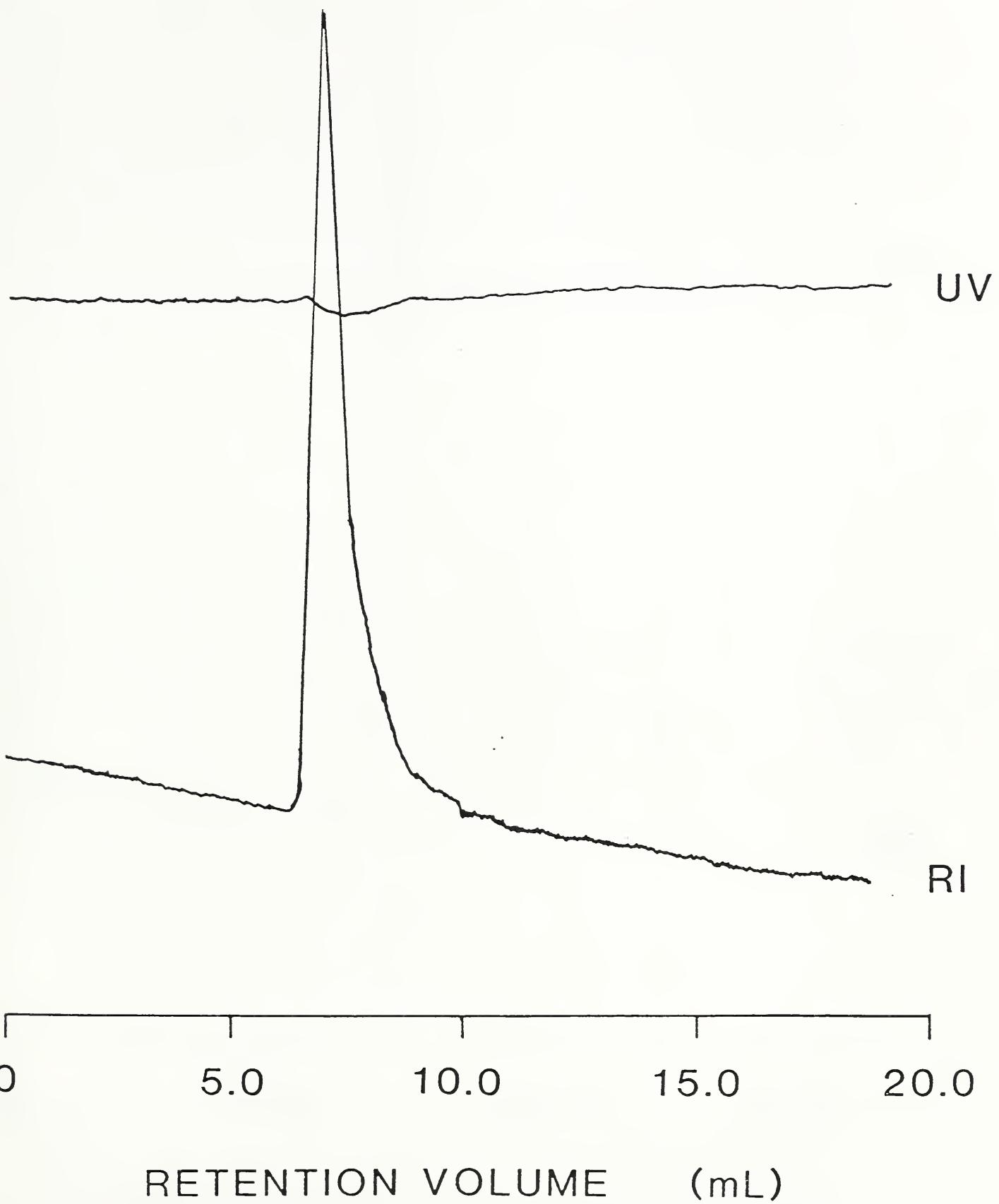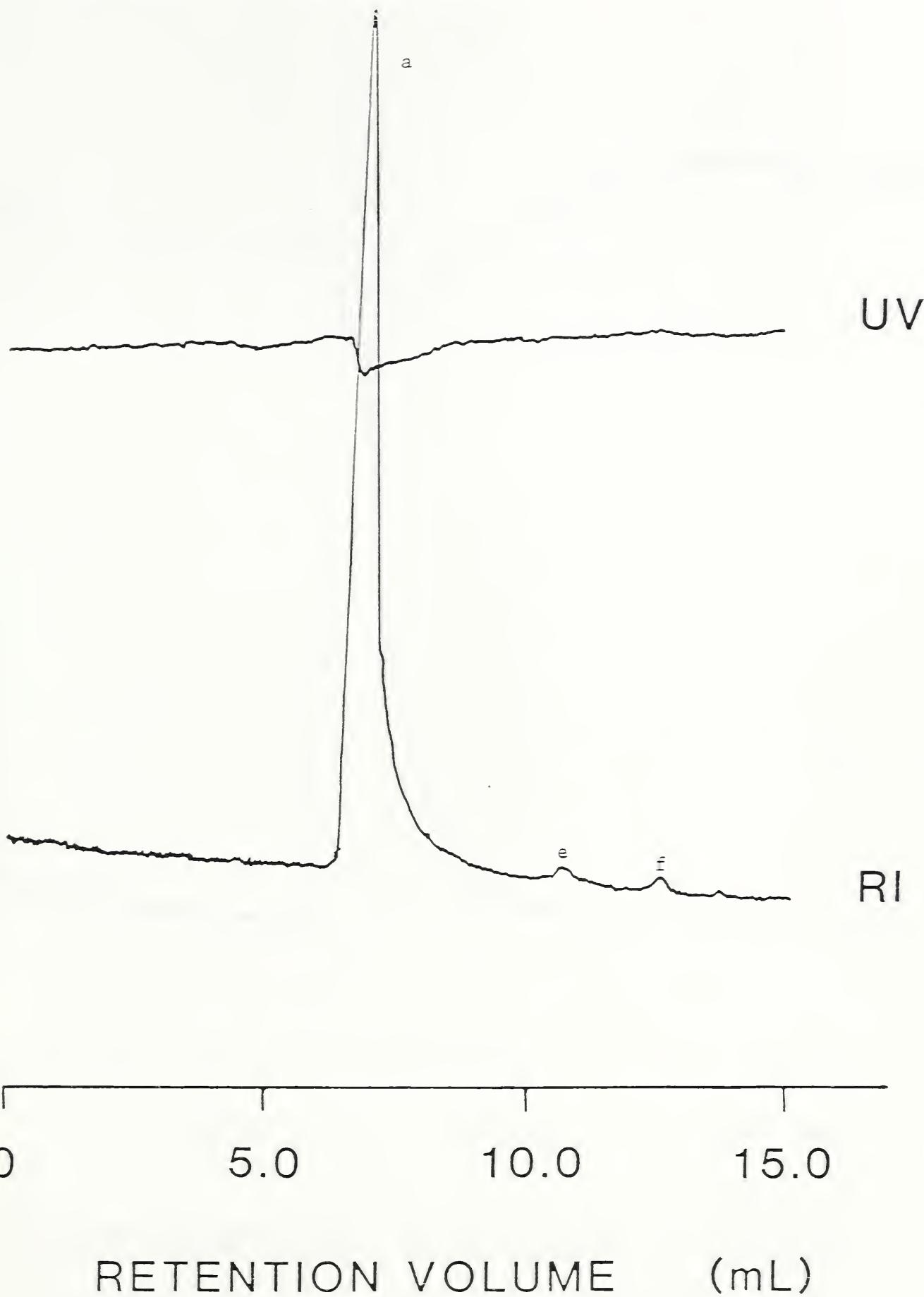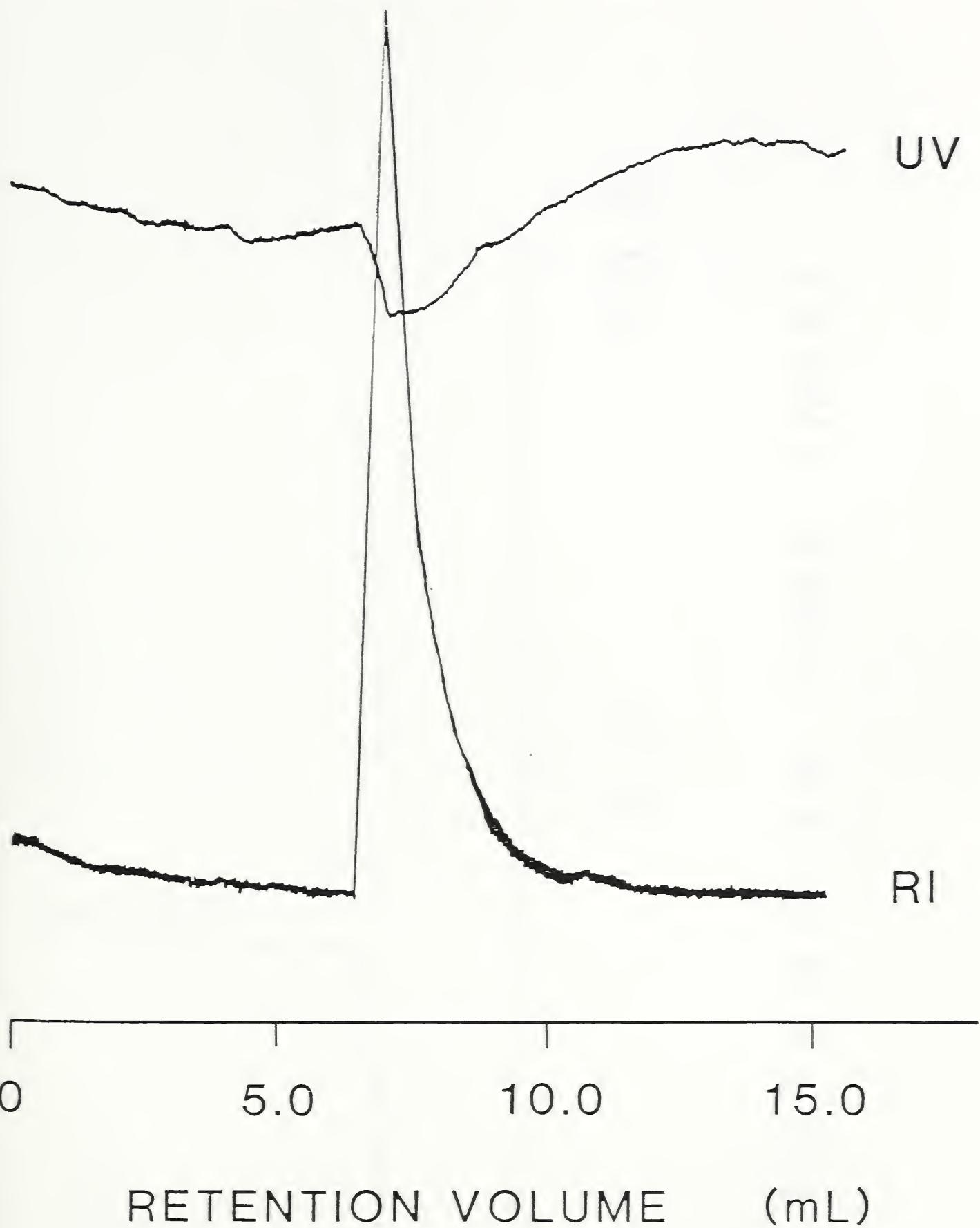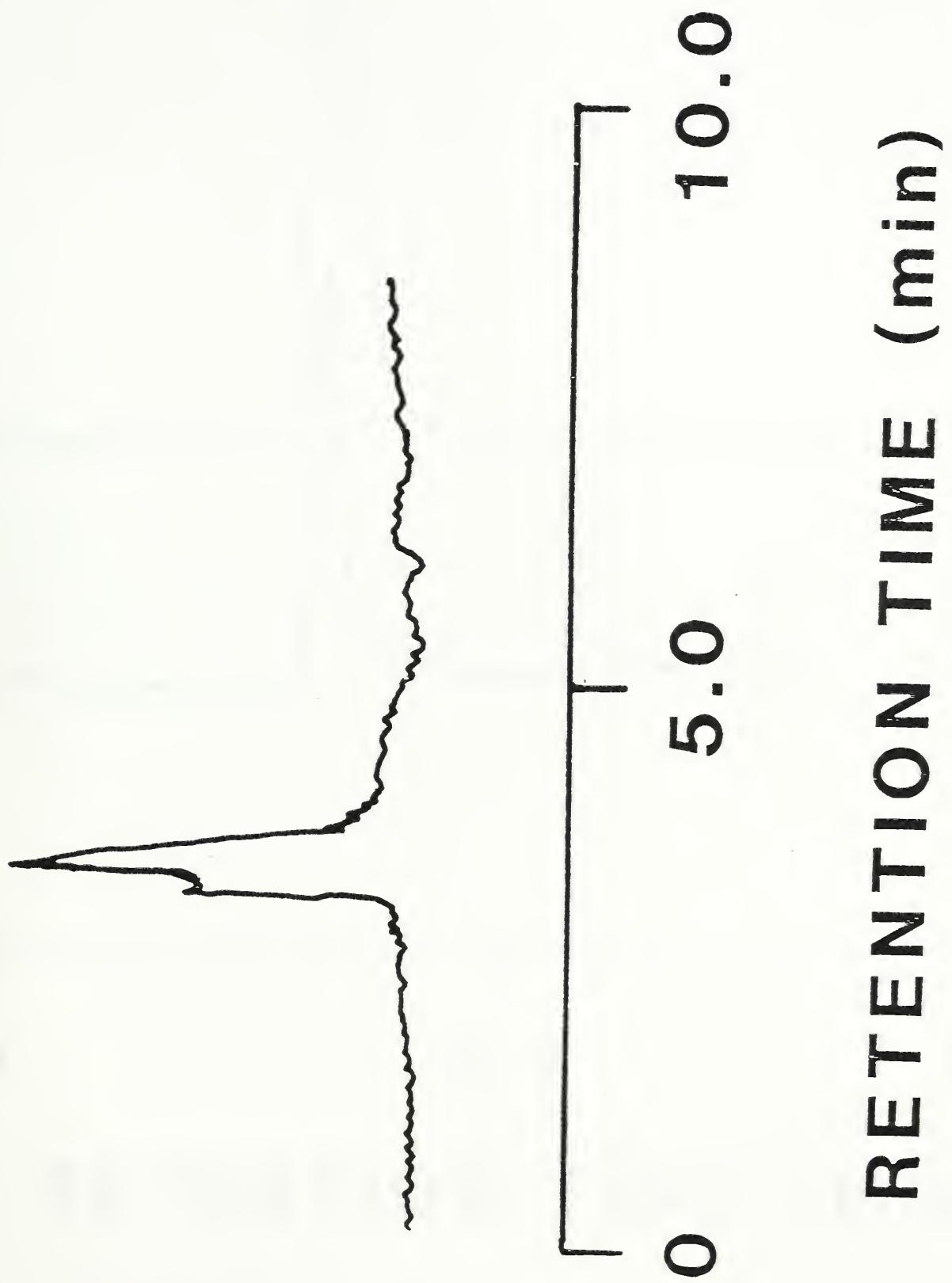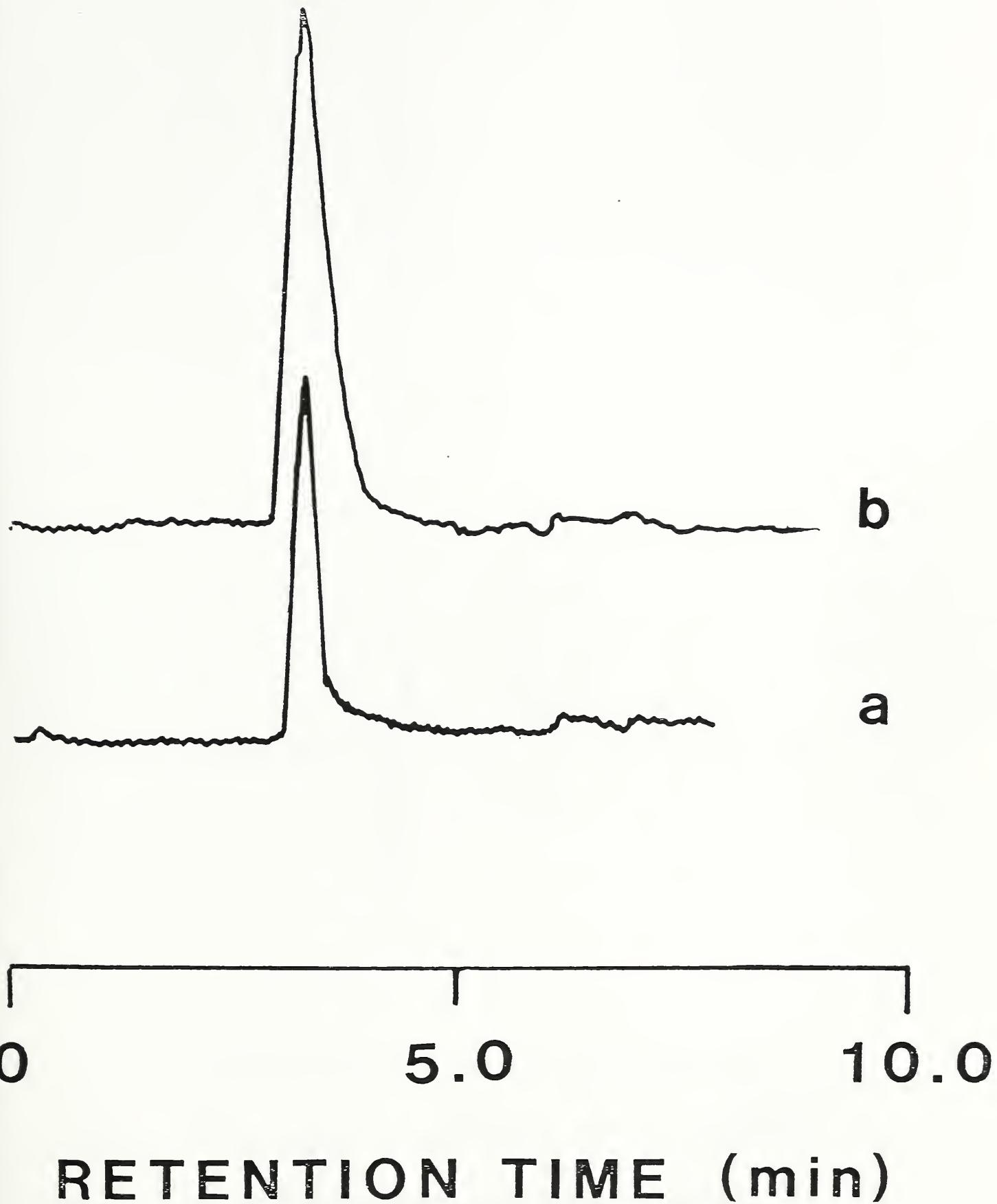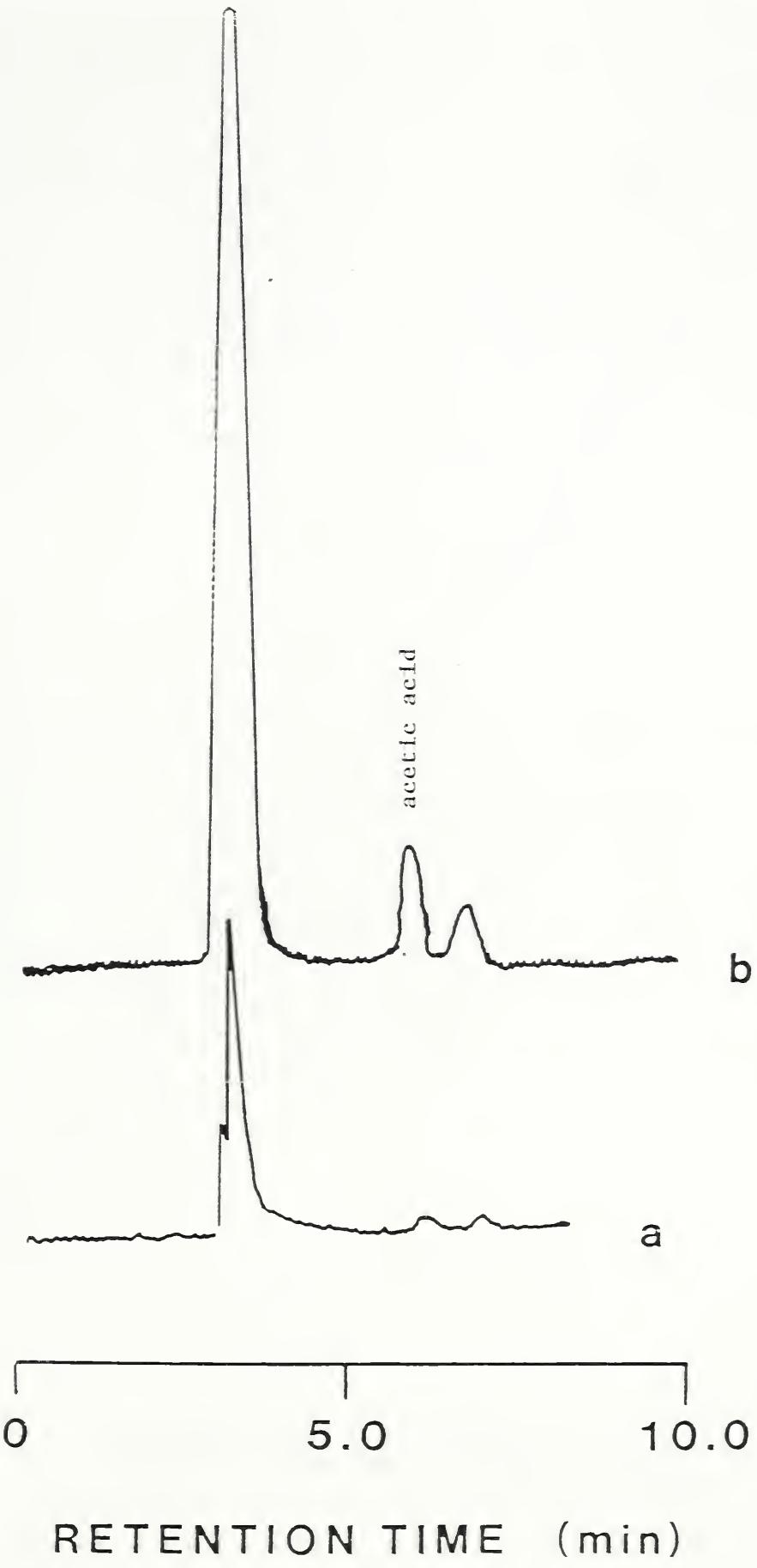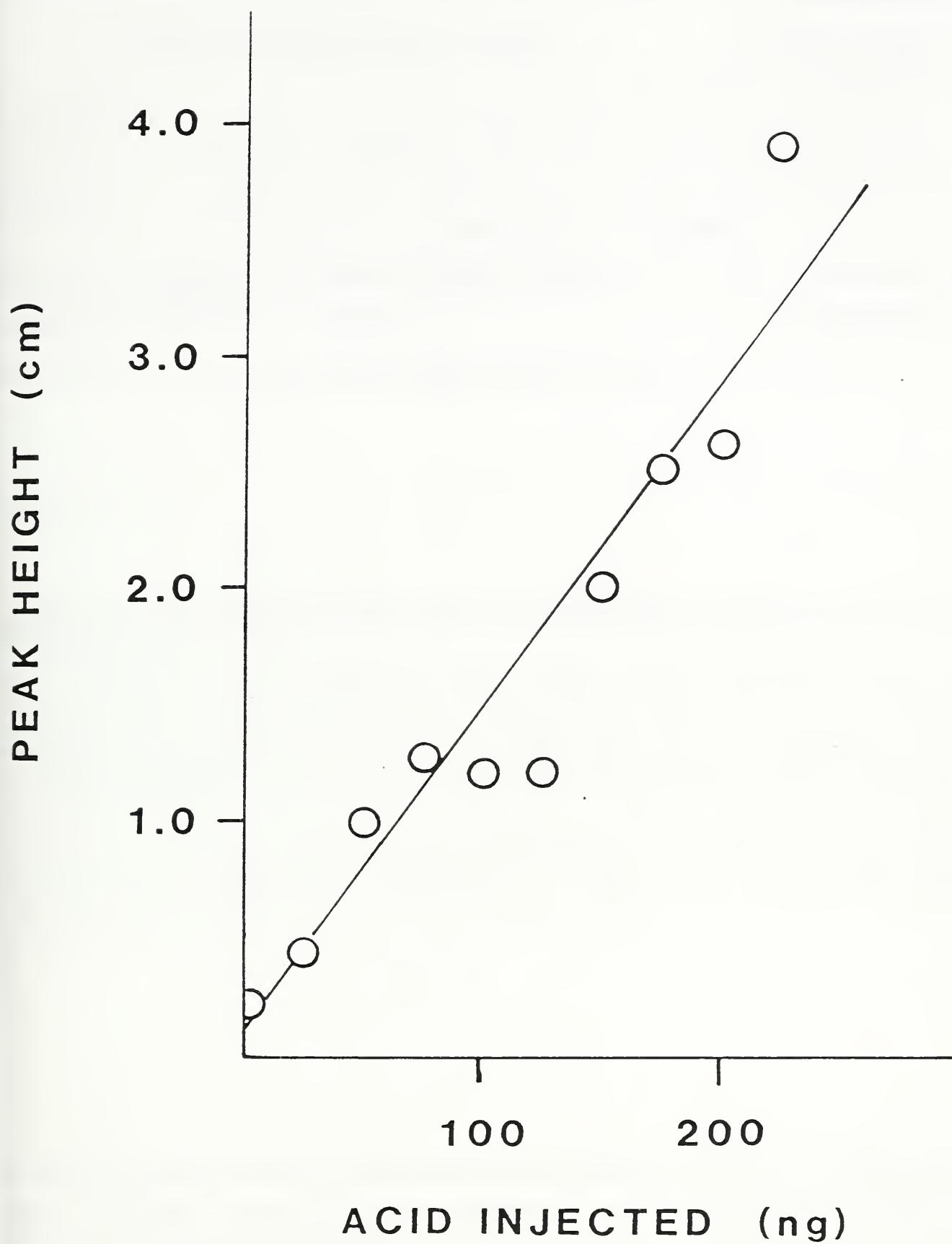
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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

We have developed methods using Mass Spectroscopy, Liquid Chromatography and Gas Chromatography to detect degradation products of rag paper and newsprint in the presence of some common air pollutants. We have searched for products that might themselves be autocatalytic to encourage degradation of these materials. In particular, we have looked at gaseous degradation products and those degradation products which are mobile and which may be transferred one paper to another by surface or gas phase diffusion.

Six organic acids have been tentatively identified as degradation products which are surface mobile on newsprint and rag paper. Acetic acid is a major organic acid gas phase component. The results of these studies were correlated with more traditional bulk paper properties tests.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

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